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The detoxification of medical waste incineration fly ash using self-propagating reaction

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Abstract

This work describes the utilization of self propagating reaction for the detoxification of the fly ash from medical waste incineration. The immobilization of heavy metals and phase transformation fly ash were evaluated. In this self propagating process, the mix ratio of fly ash to the starting mixture of more than 80% will support the self propagating process with a melting temperature of 1400℃. The toxicity characteristic leaching procedure shows that the fly ash leaching concentration of Pb, Cd exceeds the toxicity regulation level of Hazardous Waste Characteristics, and the Cu and Zn are with relatively high environmental risk too. But for the self propagating product, Cu, Pb, Cd can barely be detective in the leachate. The detoxification can be attributed to the evaporation and the immobilization process, according to the experimental analysis, the unvolatilized part is fixed in the vitrified melt inclusion, and the heavy metal speciation transform into FeMn oxides, organic matter bound and residual forms. The results indicates that melting of fly ash by self propagating reaction can be a reliably way to decrease the risk to both environment and human.

Keysords: fly ash; self-propagating; solidification; heavy metal speciation;

1. Introduction

The production of medical wastes in China is estimated to about 0.97million tons per year[1], and is becoming an important issue worldwide. Since directory landfilling is abandon since 2003[2], incineration has become a recommended way of Medical Waste Management Regulations. Incineration can reduce the original waste volume by 65-70%[3], and generates bottom ash and fly ash. Once release into the

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environment, the heavy metal and organic pollutants may damage the environment quality and human health. Thus fly ash must be properly treated to avoid secondary pollution.

The most frequent technologies of fly ash disposal include cement solidification, chemical stabilization and furnace melting[4]. In cement solidification, heavy metal is bind, ion-exchanged and absorbed onto the cement paste through hydration reaction[5]. But the addition of medical incineration fly ash delay the coagulation time above the unacceptable limit and the leaching concentration is still larger than the regulation value. Chemical stabilization extracts the heavy metal from fly ash by dissolution in acidic, alkaline or some other medium[4]. The extraction decreases the soluble metal fraction, while a great deal of wastewater is produced and needs a secondary treating facility. The ash melting process transforms fly ash into vitreous state in a melting furnace at a temperatures of 1200-1400℃for 1-2h[6]. The heavy metal leaching concentration is much lower than the values of the identification standard for hazardous wastes. Ash-melting is an extremely high-energy consumption and high investment treatment especially for medical incineration fly ash which is usually in small scale.

Self-propagating high-temperature reaction (SHR) is an exothermic chemical reaction between solid-solid or gas-solid phase[7]. The main feature of the reaction is once ignites the mixtures, the combustion wave propagates through the mixtures without additional energy. In addition to energy-saving, the reaction needs much simpler equipment and the reaction time only takes seconds[8]. Recently, the SHR has been adopted to solve environmental problem, such as of high-radioactivity waste disposal[9], organic matter degradation[10] and environmental catalysts preparation[11].

In the case of medical waste incineration fly ash, which is a combined contaminate, containing heavy metal such as Cd, Cr, Hg, Pb and persistent organic pollutant such as polycyclic aromatic hydrocarbons, Dioxin at the same time[12], SHR could be a great way for the detoxification of such compound. However, in the existed study, the mixing ratio of the medical waste incineration fly ash to the total mix is less than 30% to maintain SHR[13], the solidification mechanism and the transformation of the product is not fully described. Consequently, the effect of the composition of the medical waste incineration fly ash on the SHR needs to be further investigated.

This work investigated the thermodynamics condition of the SHR under different fly ash ratios, and the solidification effect was evaluated while maximized the waste ratio. The microstructure of the product and the solidification mechanism were also studied.

2. Materials and methods

2.1. Medical waste incineration fly ash

The medical waste incineration fly ash (MWIFA) in this study was obtained from a pyrolysis and gasification incinerator plant of medical waste in Beijing with a batch processing capacity of 40 tons per day. Fly ash samples were ball milled and sieved for particles under 150μm to ensure sample uniformity. MWIFA and reagents were mixed in the high-speed blender for 1min before SHR.

2.2. Experimental operation

In the existed studies, the solid-solid method, which involves the reduction of a metallic or a non-metallic oxide by a metal to form more stable products, is mostly adopted. The mixture of active reagent (Fe_2O_3: Mg = 40: 9, w/w) and MWIFA could only be ignited when the ratio of the MWIFA was no more than 50%. In this work, the mixture could be ignited without the Fe_2O_3 portion, which leaved the least ignited mixture to 80% MWIFA and 20% Mg, and the waste percentage thus rose greatly. Upon further exploration, the MWIFA ratio was varied from 50 wt. % to 80 wt. %, each with a 10 wt. % increase.

The tested mixture was first compressed to rectangular compacts, then put into the SHR reactor and ignited with an electrically heated tungsten wire. The reaction temperature was recorded by infrared pyrometer (Raytek 3i series, Raytek, U.S.). The reaction product was collected and milled by the high-speed blender for 2min. The products were named as FA50, FA60, FA70, FA80 according to the MWIFA addition from 50% to 80% in the SHR.

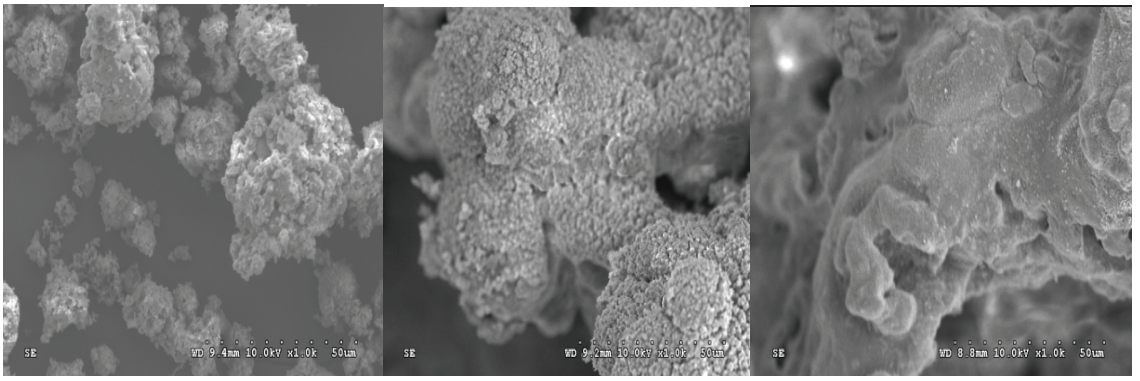
2.3. Laboratory analyses

Both of the MWIFA and the reaction product went through toxic characteristic leaching procedure (TCLP) to evaluate the potential risk of heavy metal pollution. The sequential extraction procedure (SEP) was used to examine the distribution of element species. The before and after MWIFA were characterized by X-Ray Diffraction (XRD, X'Pert PRO MPD, PANalytical, Netherlands) and Scanning Electron Microscope combined with Energy Dispersive X-ray spectroscopy (SEM-EDX, S-3000N, Hitachi, Japan).The concerned elements were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 2000, PerkinElmer, U.S.)

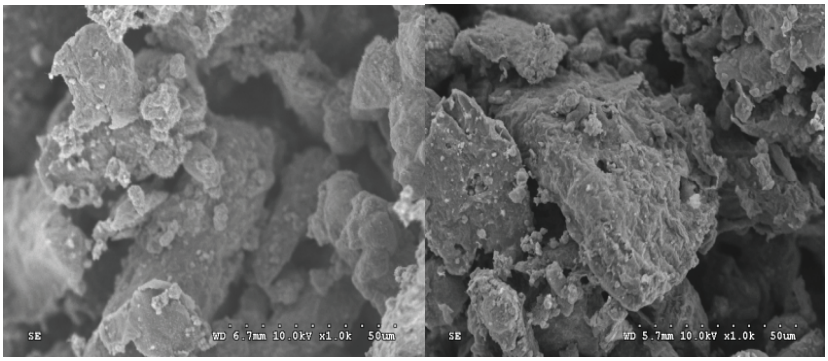
3. Results and discussion

3.1. Microstructure of origin MWIFA and SHR product

SEM image of the origin MWIFA and the SHR products at different MWIFA ratios are showed in Fig. 1. For origin MWIFA, small particles stacked loosely together, with many white-flocs covered on the surface, glass beads scattered around in the image. After the SHR, as is seen in Fig. 1b~1e, small round particles were connected through "bridges". MWIFA appeared to have been melted and condensed into a large, compact union without the white-flocs through the SHR process. This led to a smaller specific surface area and formation of solider melt inclusion, which lead to the decrease of heavy metal release in the TCLP test. When the content of MWIFA was less than 60%, the increase amount of MgO may have blocked the connection between small glass beads as small particles shown in Fig. 1d and 1e.



(a) (b) (c)



(d) (e)

Fig. 1 The microstructure of MWIFA before and after the SHR (a) origin MWIFA (b) FA80 SHR product (c) FA70 SHR product (d) FA60 SHR product (e) FA50 SHR product

3.2. The mineral composition and transformation

The XRD results in Fig. 2 demonstrated that the major mineral phase of MWIFA was NaCl, while according to the XRF results, some other major elements, e.g. Ca, Si, Al, Fe, were not revealed through the XRD patterns. This probably dues to the diversification of the mineral formation for each element, or most of the components in MWIFA are amorphous. As is showed in Fig. 2, the relative intensities of NaCl peaks decrease greatly from original MWIFA to the SHR products. The appearance of Mg peak in FA50 indicated the redundant Mg under this ratio. The degrees of crystallization from FA to FA50 are 46%, 27%, 18%, 24% and 24%, repectively, which verifies the observation of the formation of amorphous phase melt inclusion in Fig.1.

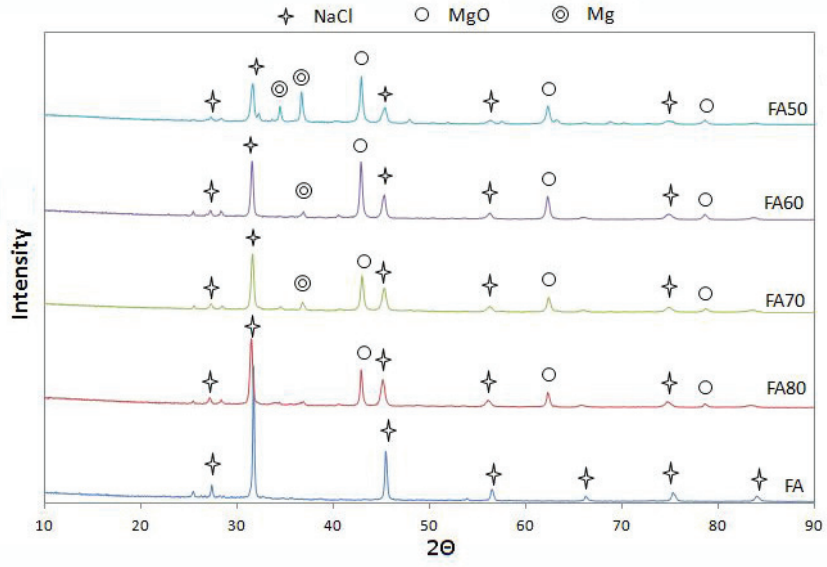


Fig. 2 XRD results of the origin MWIFA and SHR product at different ratios

3.3. TCLP results

The TCLP is used to evaluate the potential release of heavy metal from MWIFA. As was showed in Table 1, the leaching concentrations of MWIFA meet neither the US nor the Chinese TCLP standards, thus MWIFA can be characterized as hazarders waste. The leaching concentration of Pb, Zn, Cd exceed 28, 22, 6 times of the standers respectively, and Cu is quite close to the limit of Chinese standers, thus the most concerned heavy metal elements are Pb, Zn, Cd and Cu in this study.

After the SHR, most of the heavy metal became undetectable, except for Pb and Zn, which were at very low concentration too (under 0.1 and 1 respectively). The MWIFA leaching concentration decreased vastly after the SHR and was able to fulfill the standard for hazardous wastes.

The origin MWIFA absorbed a lot of fine particles and volatile heavy metals on the surface, which easily release into the leachate. The silicates fundamental units of glass beads were formed tetrahedronly by four O^{2-} with a Si^{4+} at the center. The O^{2-} on the silicate tetrahedron was able to connect with one more Si^{4+} on the other silicate tetrahedron and form an endless silicate network. During the SHR, the glass beads were melted and formed into a solid solution. The Si-O network of origin glass beads broke, the heavy metals or heavy metal irons evenly distributed in the oxygen-silicon tetrahedron. The lower valence metal iron such as Na^{+}, K^{+}, Ca^{2+} acted as network modifiers and filled in the gaps of oxygen-silicon framework; while some other irons such as Al^{3+}, Mg^{2+}, Zn^{2+}, acted as network intermediates, which can replace Si^{4+} in the network and also filling in the gaps. In summary, the heavy metal irons were enclosed in the silicate frameworks, resulted in low leaching concentration.

Table 1 TCLP leaching concentration of origin MWIFA and SHR product at different ratios (mg/L)

Samples	As	Cd	Cr	Cu	Ni	Pb	Zn
FA80	ND	ND	ND	ND	ND	ND	0.08
FA70	ND	ND	ND	ND	ND	ND	0.13
FA60	ND	ND	ND	ND	ND	0.069	0.14
FA50	ND	ND	ND	ND	ND	0.025	0.81
Origin FA	0.4	6.02	0.15	79.45	0.77	142.54	2216.87
US standers	5	1	5	-	-	5	-
Chinese standers	5	1	5	100	5	5	100

3.4. The variation of heavy metal speciation

The sequential extraction procedure was used to determine to variation of heavy metal speciation before and after the SHR (Fig. 3). In origin MWIFA, about 90% of the Cd were exchangeable or bound to

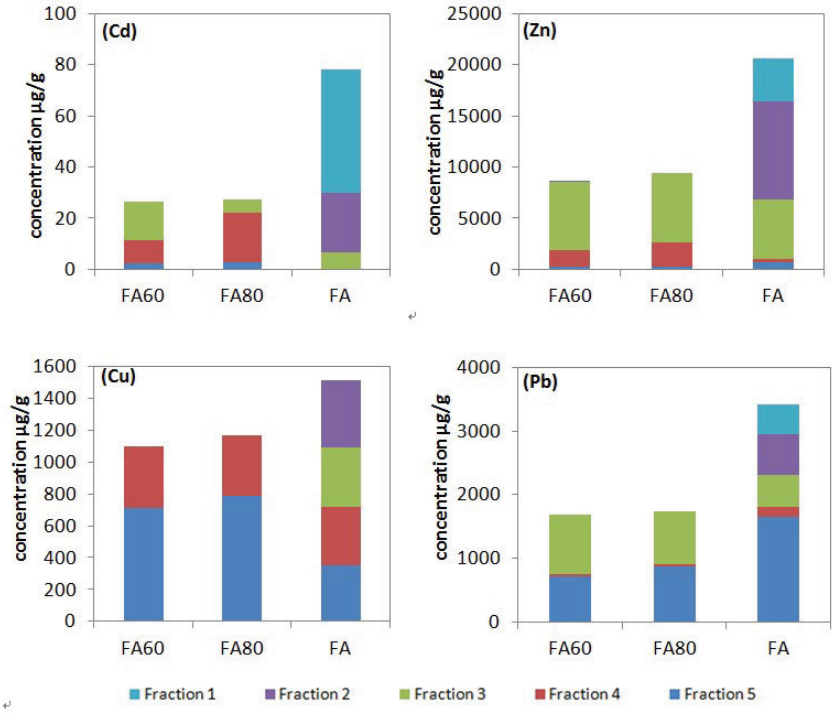


Fig. 3 Fraction element distributions of MWIFA and the SHR product at different ratios

carbonates, leading to high leaching concentration in TCLP. After the SHR, Cd from Fraction 1 and 2 transformed to iron and manganese oxides or organic combination state except for the evaporation part. Zn in origin MWIFA concentrated on Fraction 1, 2 and 3, after SHR, the content of Fraction 3, 4 increased slightly. This indicated that the decrease of leaching concentration was mainly because of the evaporation of Zn. Cu equally distributed in Fraction 1, 2, 3, 4 in MWIFA. The volatilized during SHR was relatively small, Cu in Fraction 5 tremendously increases, thus the solidification of Cu mainly attributed to the melt inclusion. Cu was fixed in the silicate framework, benefits in low leachability.

The sequential extraction procedure can also explain the differences of leaching concentrations of each element. The leachability of each element was related to their content and speciation distribution in MWIFA (Fig. 3). The leaching concentrations were consistent with the total content of the heavy metal, that is Zn>Pb>Cu>Cd.

4. Conclusion

The SHR is a reliable technique for the detoxification of the heavy metals in MWIFA. Most of the heavy metals were not detectable in treated MWIFA. The detoxification was attributed to the solidification and the evaporation of heavy metals. The unvolatilized parts of heavy metal transform into FeMn oxides, organic matter bound and residual forms from exchangeable and carbonates phase, which are stable in acid environment. The XRD and SEM results indicated that MWIFA was melted and turned into melt inclusion. The degree of crystallization drop to 18% from the origin 46% illustrated the vitrification of the MWIFA. Heavy metals were mounted in the silicate framework, which led to the tremendous decrease in leaching concentration.

Acknowledgements

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